

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A206 515

## REPORT DOCUMENTATION PAGE

Form Approved  
OASD No 0704-0108  
Exp Date Jun 30, 1985

1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT <b>Approval for Public Release: Distribution unlimited.</b>		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) <b>NATICK/TR-89/022</b>			7a. NAME OF MONITORING ORGANIZATION		
6a. NAME OF PERFORMING ORGANIZATION <b>U.S. Army Natick Research, Development &amp; Engineering Center</b>		6b. OFFICE SYMBOL (if applicable) <b>STRNC-YSM</b>	7b. ADDRESS (City, State, and ZIP Code)		
6c. ADDRESS (City, State, and ZIP Code) <b>Kansas St., ATTN: STRNC-YSM Natick, MA 01760-5020</b>		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS			
8c. ADDRESS (City, State, and ZIP Code)		PROGRAM ELEMENT NO. <b>611101</b>	PROJECT NO. <b>91A</b> <b>1L161101A-</b>	TASK NO. <b>07</b>	WORK UNIT ACCESSION NO. <b>142</b>
11. TITLE (Include Security Classification) <b>The Effects of Supercritical Fluids on High Performance Polymers.</b>					
12. PERSONAL AUTHOR(S) <b>Rerry, David and Levasseur, Leonard A.</b>					
13a. TYPE OF REPORT <b>Final</b>	13b. TIME COVERED <b>FROM 10/85 TO 9/87</b>	14. DATE OF REPORT (Year, Month, Day) <b>1989 February 28</b>		15. PAGE COUNT <b>39</b>	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	<b>Super Critical ) Yarns Dyes ) Polymers )          Ballistic ) Extraction )          Tensile Strength ) Liquid Phase ) Gas Phase . (right) ←</b>		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>High performance polymers in current use have achieved a remarkable degree of ballistic protection. In spite of this achievement the performance characteristic of many of these polymers falls considerably below theoretically predicted levels. There is considerable room for improvement in the properties of ballistic polymers in terms of chemical design, morphology, and fabrication changes for existing and new polymer structures. The project objective is to investigate the process of using supercritical fluids (SCF) to expand the parameters available for fiber fabrication or polymer modification with the aim of improving the performance properties of existing polymeric materials. Specifically, the research is intended to explore various aspects of SCF technology in order to form a basis from which further research on enhancement of ballistics properties can be accomplished. This preliminary study, therefore, is not comprehensive but it identifies areas of high potential for further work.</p>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>		
22a. NAME OF RESPONSIBLE INDIVIDUAL <b>Leonard Levasseur</b>			22b. TELEPHONE (Include Area Code) <b>(508) 651-5492</b>		22c. OFFICE SYMBOL <b>STRNC-YSM</b>

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## PREFACE

The results described in this final report were obtained under an In-house Laboratory Independent Research project entitled "Relationship of Molecular Structure/Conformation to Performance of Ballistic Polymers". The project was initiated 1 October 1985 and completed 30 September 1987. The project data are contained in Natick note book number 7821. The authors wish to thank R. Shuford and T. Murray of Materials Technology Laboratory, Watertown, MA, for technical assistance and for loan of the supercritical fluid flow apparatus. Also the assistance of M. Mahar and W. Koza for static tensile tests and ballistic impact tests is gratefully acknowledged.

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# The Effects of Supercritical Fluids on High Performance Polymers

## I. INTRODUCTION

### A. Background

High performance polymers in current use have achieved a remarkable degree of ballistic protection. In spite of this achievement, the performance characteristics of many of these polymers fall considerably below theoretically predicted levels<sup>1</sup>. There is considerable room for improvement in the properties of ballistic polymers in terms of chemical design, morphology, and fabrication changes for existing and new polymer structures.

Presently high performance fibers are solution spun from polymers that are nearly intractable. The aromatic polyamides, which are solution spun from concentrated sulfuric acid, are an example. The range of suitable solvent systems and conditions for spinning these fibers is obviously limited and there is little opportunity to improve fiber properties beyond what has already been achieved during the spinning process with conventional technology.

## B. Objective

The project objective is to evaluate approaches to using supercritical fluids (SCF) as a route to expanding the parameters available for fiber fabrication and improving the performance properties of existing polymeric materials. Specifically, the research is intended to explore various aspects of SCF technology in order to form a basis from which further research on the enhancement of ballistic properties can be accomplished. This preliminary study, therefore, is not comprehensive but it identifies areas of high potential for further work.

## C. Supercritical Fluids, Background<sup>2,3</sup>

Supercritical fluids are either solvents or solvent/solute combinations that have been subjected to conditions of temperature and pressure beyond their critical point. A way of physically representing this phenomenon is to consider an enclosed (constant volume) container that contains a liquid and its vapor. As the temperature of the liquid is increased the pressure and density of the system including the vapor above the liquid increases. At sufficiently high pressure the density of the vapor above the liquid increases to the point where it equals that of the liquid. At this point, the critical point, there is no boundary or phase distinction between the liquid and the vapor and the material in the container is commonly described as a fluid. The fluid does not exhibit the properties of a true liquid or a vapor; however, it possesses properties of both phases.

Fluids above their critical point show very large changes in density with very small changes in pressure. The solvent power of a supercritical fluid is a direct function of its density and it should, in theory, be possible to obtain conditions of high solubility with only small changes in the pressure of the system. Additionally, the viscosity and diffusivity properties of supercritical fluid systems are more like those of a gas than a liquid and attainment of equilibrium solvation is more rapid under these conditions.

The temperatures and pressures required to reach the critical point for many solvents are not unreasonably high (Table 1). One factor that should be borne in mind is that the critical constants of these solvents may change as the composition of the system (solute/solvent) changes and it would then be necessary to make changes in the physical parameters to preserve the supercriticality of the system.

Table 1  
Critical Temperatures and Pressures  
for Various Solvents

Solvent	Temp °C	P(psig)
Freon 23	26.9	690
Carbon dioxide	31.0	1072
Nitrous oxide	36.5	1054
Ethylene	9.9	742
Argon	-122.3	706
Acetonitrile	275	698
Methanol	240	1154



#### D. Three Approaches

Our approach has been to examine the ability of a variety of supercritical fluids to interact with various high polymers, prepolymers and monomers. The aim is to develop information about the parameters necessary to dissolve, extract, and polymerize these materials in an attempt to improve ballistic properties. The approach focuses on three major lines of investigation.

The first is to determine whether various polymeric materials can be solubilized by treatment with supercritical fluids. If this is feasible, it might be possible to dissolve even relatively intractable polymers, such as those used for the various aramids (e.g. Kevlar<sup>(R)</sup>), and solution spin fibers from the supercritical fluid. This technique would allow considerable latitude in selection of the fiber spinning parameters.

A second area of investigation is to examine whether extraction under supercritical fluid conditions can lead to changes in the tensile properties of existing fibers and fabrics. Possibly, the removal of low molecular weight materials, monomers and oligomers, would allow better orientation of the main polymer chains and lead to increased performance. It is unknown and must be determined whether this type of treatment might be expected to reduce free volume within the polymer and lead to decreased tensile strength under impact loading. If, in fact, an extractive process does decrease the performance properties of the fiber, it would be worthwhile to investigate whether lubricating additives could be added by the supercritical fluid process to increase free volume.

The third area to be investigated is whether actual polymerizations can be carried out while the reactants are in the supercritical state. With this technique premature precipitation of the developing polymer chains would be prevented, thereby increasing molecular weights and producing narrow molecular weight distributions. As with other aspects of supercritical fluid interaction with polymers, very little work has been done in this area. Only recently was the first report of a polymerization reaction in a supercritical fluid reported<sup>4</sup>. Free radical polymerization of polystyrene was conducted in supercritical ethylene. The experiment permitted control of chain growth and precipitation rates. With our supercritical fluid system it would be interesting to determine if various condensation polymerizations can be carried out. This research is expected to lead to the formation of polymer/solution dopes of polyamides and other polymer types that might be useful for direct spinning of high performance fibers.

## II. SUPERCRITICAL FLUID FLOW EXPERIMENTS.

### A. Apparatus

The apparatus used for supercritical fluid flow experiments is diagramed in Fig. 1. In all of the preliminary experiments described in this report, carbon dioxide (Med-Tech, Tank #CX-1788) was used as the fluid. Liquid carbon dioxide was led from a tank through a heated tube to a pump (Superpressure Inc., Silver Spring, MD, Catalog No. 46-13421). The pump was capable of developing pressures with either liquids or gases up to 10,000 psi. Control of the pump was by an electrical relay that was actuated by a pressure gauge located between the sample cell and the vent trap. The outlet from the pump was led through high pressure stainless steel tubing to a surge tank, which was externally heated by heating cables. The temperature of the surge tank was adjusted so that the conditions inside the surge tank were above the critical point for the solvent in use. This insured that the fluid entering the sample cell, which was attached to the surge tank with heated stainless tubing, was at or above the critical point when it entered the cell.

The sample cell was a threaded stainless steel cylinder (Autoclave Engineers, Inc., 20F-16463, 800-0646, M.A.W.P. 20,000 psi, 316-SS) capped at each end. It had an inside diameter of 15mm and length of 200mm and was externally heated. The exit of the sample cell led into a vent trap which allowed for collection of extracted material where appropriate. The effluent of the trap ran through a flow meter that could provide a reading of total gas flow for the run. The final exit of the system was into a fume hood.

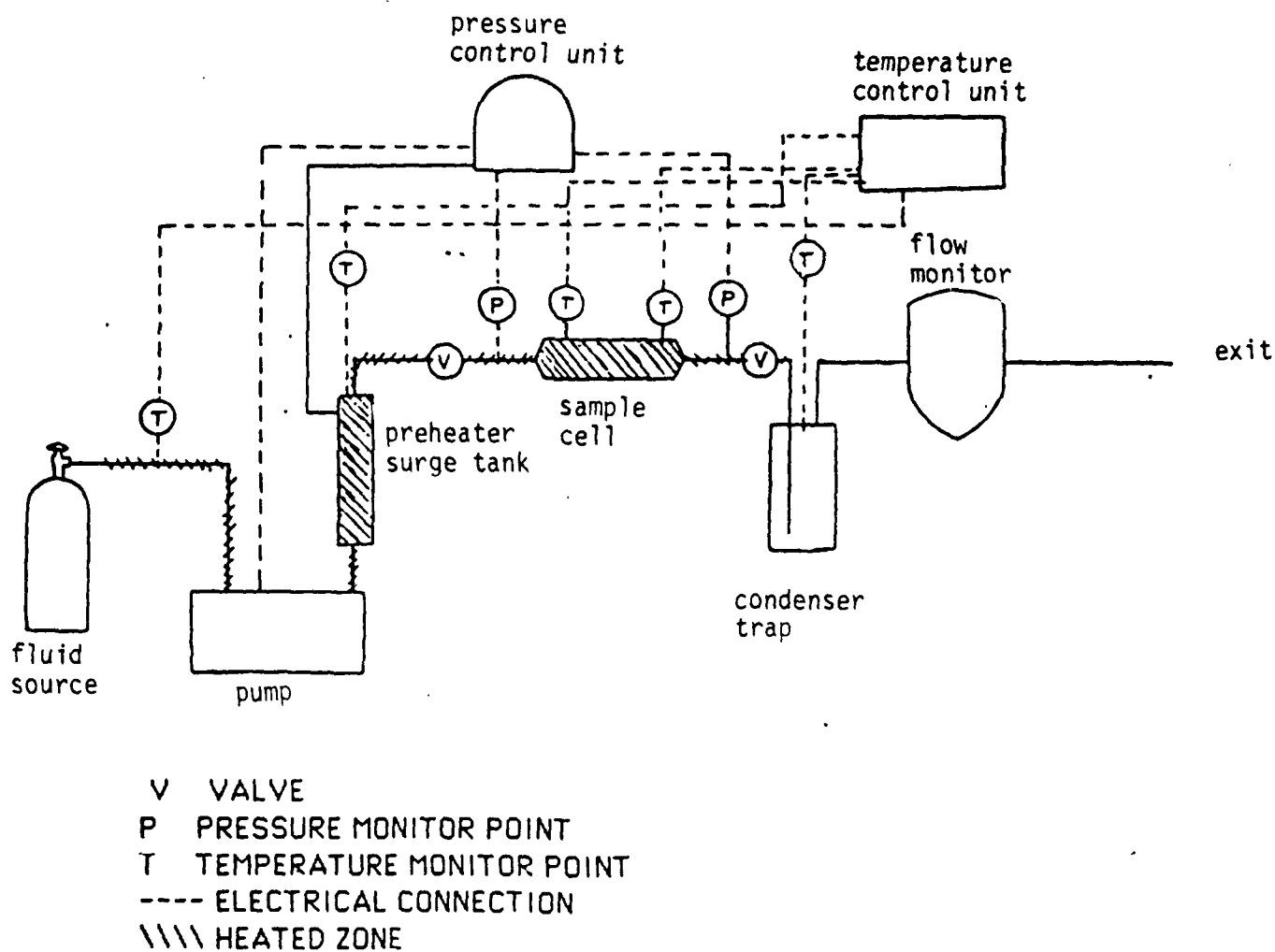


Figure 1. Supercritical fluid flow apparatus.

## B. Supercritical Fluid Extraction Procedure for Fibers.

The extraction procedure for fibers was as follows. In a typical run the sample, 1-2 g in the form of a yarn wound onto a strip of aluminum foil, was weighed and then placed into the sample cell. Supercritical carbon dioxide at 900-1200 psi was introduced into the cell, which was maintained at 40-50°C. The SCF carbon dioxide solvent was allowed to slowly bleed into the vent trap during a six hour period. After the run the sample was again weighed, conditioned to standard temperature and humidity, and break tested using a procedure discussed later. No significant amount of residue was noted in the vent trap for any of the runs.

## C. Materials Used

Two samples of Kevlar, a fully aromatic polyamide fiber, were provided by DuPont:

Kevlar-29 yarn, 1500 denier, old, and

Kevlar-29 yarn, 1500 denier, new.

The differences between old and new samples were somewhat obscure. It has been noted by workers at the Individual Protection Directorate (IPD) Natick, that older samples of Kevlar may have been prepared by a slightly different spinning process than more recent material. The predominant manifestation of the suspected differences in these samples was increased tensile strength for the new Kevlar material. It was unknown whether the tensile difference was due to an ageing effect or was an inherent property

of the material at the time of fabrication. It was of interest to determine whether SCF extraction would have an effect on the two types of materials.

#### D. Static Tensile Testing<sup>5</sup>

Tensile testing was conducted on an Instron Tensile Tester using a 0-100 lb cell fitted with Kallaway Clamps. Tests were run on 10 inch samples of yarn drawn at a rate of 12 inches per minute<sup>5</sup>. The tensile testing results are summarized in Table 2. The values given in the table are the averages of five tests.

Samples of early production 1500 denier Kevlar yarns were extracted under identical SCF conditions using carbon dioxide as SCF, Pressure: 900-1200 psi, Temperature: 40-50°C and six hour extraction time. A difference was noted between the early production and current production samples when extracted with the same conditions. The current material was essentially unaffected by the extraction, but the early material showed considerable decrease in breaking strength.

TABLE 2

#### Static Breaking Tests for Kevlar-29

##### Initial Experiments

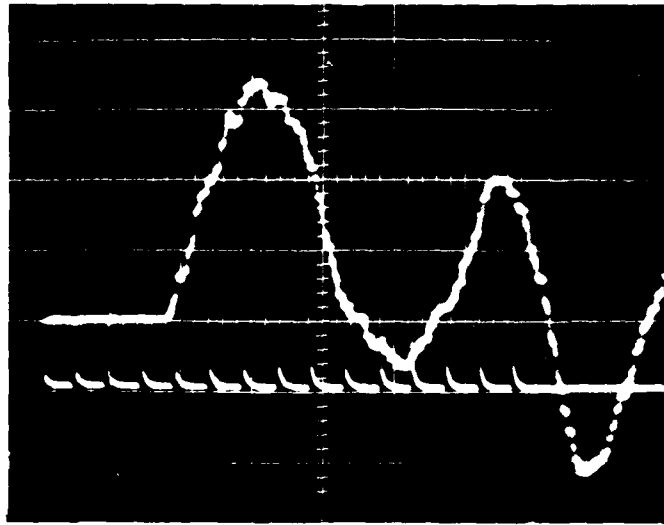
Run #	Sample	<u>Breaking strength</u>		
		control	extracted	%change
1.	Kevlar-29 1500D (old)	49.4	48.1	-2.6
2.	Kevlar-29 1500D(new)	57.7	57.3	-0.7

#### E. Ballistic Testing of Kevlar Yarns.

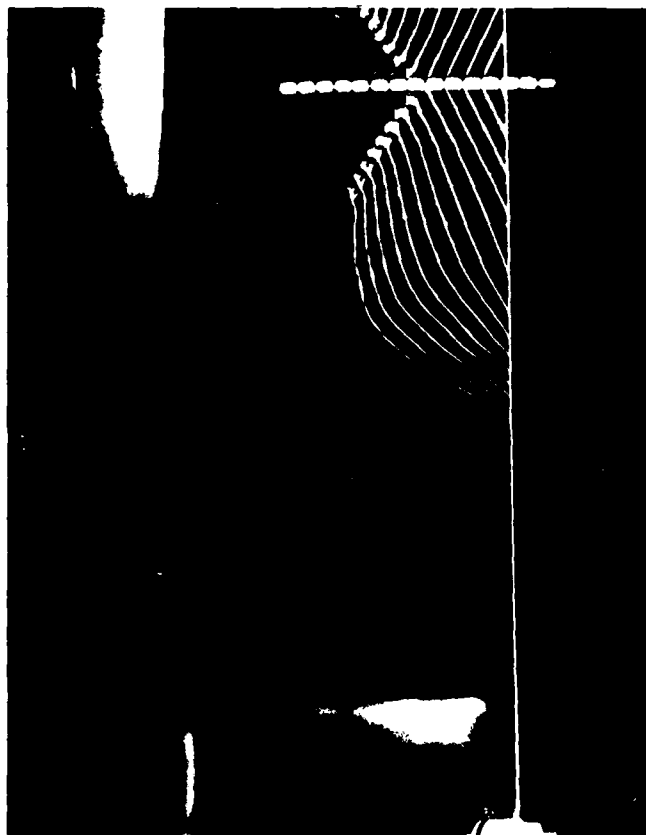
Ballistic properties of early and current production Kevlar-29 samples were measured by the Individual Protection Directorate<sup>6</sup> (IPD) on material before and after SCF extraction with carbon dioxide. The results of these tests are presented in Table 3 and the actual stress strain curves and impact data for new Kevlar-29 yarn are presented in Fig. 2.

TABLE 3  
Ballistic Properties of Kevlar-29 Samples

<u>Fiber Type</u>	<u>Unextracted</u>	<u>Extracted</u>	
	"Old Control"	"New" Run 4	"Old" Run 3
Yarn Size, Denier	1520	1530	1515
Impact Velocity, m/s	312.7	313.5	313.5
Breaking Tenacity, g/Den	10.1	11.3	12.0
Breaking Elongation, %	2.5	2.6	2.3
Time to Break, micro s	125	125	125
Strain Wave Velocity, m/s	6770	6770	6770



Oscilloscope trace of yarn: Force vs. Time



High speed photograph of impacted yarn used in measurement of yarn: Extension vs. Time

Figure 2. Ballistic stress-strain curves.



The results of the ballistic impact tests (Table 3) show slight increases in the breaking tenacity for the "old" extracted sample and a slight decrease in elongation. It remains to be determined whether these values based on a single test are a valid representation of the properties of the whole sample.

### III. SUPERCRITICAL FLUID STATIC EXPERIMENTS

#### A. Apparatus

In order that a range of solvent systems could be screened rapidly and efficiently with various polymers, it was advantageous to make use of an apparatus that did not rely on an external flow concept. A 600 mL Parr Pressure Reactor was adapted by removing the stirring paddle and inserting a solid plug into the stirrer opening. A stainless steel condenser loop was setup inside the chamber. When air was passed through the loop the supercritical fluid in the reactor became more dense due to cooling and was directed onto a sample held in a sintered glass filter funnel. The sample could then be continuously extracted with the supercritical fluid.

#### B. Procedure.

The polymer sample was weighed and added to the sintered glass funnel.

The sample was placed into the reactor chamber and approximately 75 mL of solvent was added. Methanol was the only solvent used for the preliminary runs. After addition of the polymer and solvent, the reactor was sealed and heated to the critical point of the solvent while air was blown through the condenser loop. After the run time was over, the reactor was cooled, opened, and the contents were evaluated qualitatively for solubilization of the polymer.

#### C. Materials

The following materials were weighed and placed into the reaction chamber.

Nylon 6,6:

Pellets

Aldrich Chemical Co. (#18,112-9)

Nylon 6:

Pellets

Aldrich Chemical Co. (#18,111-0)

Kevlar Fabric

#### D. Sample Treatment Schedule.

The treatment schedule for the samples is listed in Table 4.

TABLE 4

## Static Treatment Conditions

#	Sample	Wt.(g)	Press.(psi)	Temp.(°C)	Time (h)
1.	Nylon 6,6	4-5	1000	250	2
2.	Nylon 6,6	1.08	1000	245-252	2
3.	Nylon 6	1.66	1120	250	2
4.	Kevlar Fabric	1.44	1100	250-255	14

## E. Results and Discussion, Phase I

The results of Run 1. were inconclusive because parts of the reaction chamber's bomb head were contaminated. A hard grey-brown residue was left in the filter funnel that had contained the sample, and we presumed that this had come from the contaminated bomb head and not from the polymer. Run 2 was essentially the same as Run 1 except the bomb head was cleaned and a smaller sample was used. The results from this run were unexpected in that all of the polymer sample had been dissolved by the methanol and a brown filtrate remained in the bottom of the reactor. The filtrate had a strong odor of amine and subsequent tests indicated that methanolysis of the polymer had taken place.

This is an unusual reaction for amides, especially polyamides. If, in fact, complete methanolysis of the polymer has been achieved this fact has important implications for polymer reprocessing. Degradation of a condensation polymer such as a polyamide to its monomer by a simple and efficient process would be very useful for recycling these polymers. It may also be possible with this process to degrade mixtures of waste polymers or copolymers (e.g., amides, esters, etc.) to their monomers, then separate the monomers and repolymerize them into useful materials.

A similar result was observed for nylon 6 (Run #3). The entire sample was dissolved and a golden-brown solution resulted with a slight amine odor. In this case the methanolysis product expected is the amino-ester of the original monomer.

The Kevlar fabric sample was considerably more resistant to supercritical methanol. Only 1.5% of the sample was extracted under considerably more severe conditions. However, even in this case an amine odor was noticed, which may have been due to the formation of para-phenylenediamine. (See section IV, below, on depolymerization.)

#### IV. PHASE II WORK.

##### A. Yarn Extractions with Freon<sup>(R)</sup> and Carbon Dioxide.

Extractions of high tensile yarns were continued with ultra-high-density polyethylene (UHDP). Spectra 900<sup>(R)</sup> fibers made of UHDP were extracted with Freon 23 (Fluoroform) in the Parr bomb apparatus and with carbon dioxide in the flow apparatus in order to determine whether pregelation of the fiber could be achieved.

Spectra fibers were wound around a sample holder frame. The sample was placed into the reactor bomb, sealed, and cooled in dry ice/acetone. The Freon was then allowed to condense in the cooled bomb over a 15 minute period. The Freon cylinder was disconnected and the bomb was heated to its critical temperature, 30°C. The pressure rose above the critical point to 700 psi and was held for approximately an hour. It was then cooled to room temperature and excess pressure released.

After treatment the fiber samples were visually unchanged. They were then tensile tested. The test data indicated a slight increase in breaking strength over the control sample (Table 5).

Spectra 900 and Spectra 1000<sup>(R)</sup> fibers were also extracted with carbon dioxide at low and high temperatures. The conditions used were 40-50°C and 900-1200 psig for the low temperature extractions and 80-90°C and 1800-2100 psig for the high temperature extractions. No visible changes were observed in the extracted fibers. Tensile testing data are shown in Table 5.

Photomicrographs were obtained for these fibers in order to investigate whether gelation had occurred. The photomicrographs of the carbon dioxide treated Spectra fibers showed no significant changes. It was of interest to note the banding features that occurred periodically along the fibers. The bands look like kinking in a surface coating on the fiber; however, they are more probably due to effects caused by the spinning process. No other evidence of a coating was found for the fibers.

TABLE 5  
Break Strength for Fibers Extracted  
with Carbon Dioxide and Freon

<u>Sample</u>	<u>control</u>	<u>extracted</u>	<u>Diff. %</u>
Spectra 900 -Freon 23	55.9	57.3	2.5
Spectra 900-CO <sub>2</sub>	51.3	56.0	9.2
Spectra 1000-CO <sub>2</sub>	24.0	26.3	9.6
Spectra 900 Naphthalene	55.9	57.8	3.4



Figure 3. Untreated Spectra 1000.

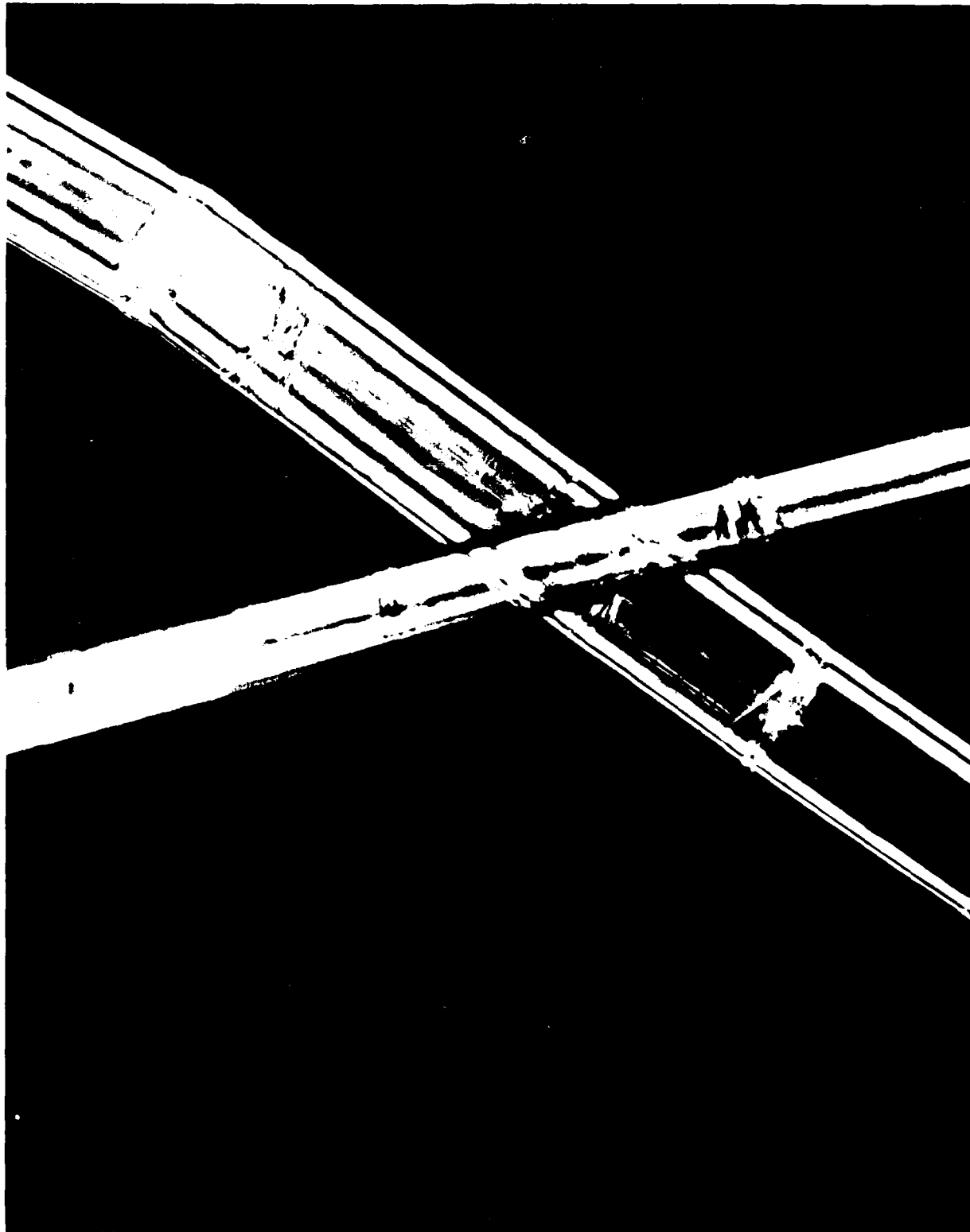


Figure 4. Extracted Spectra 1000.

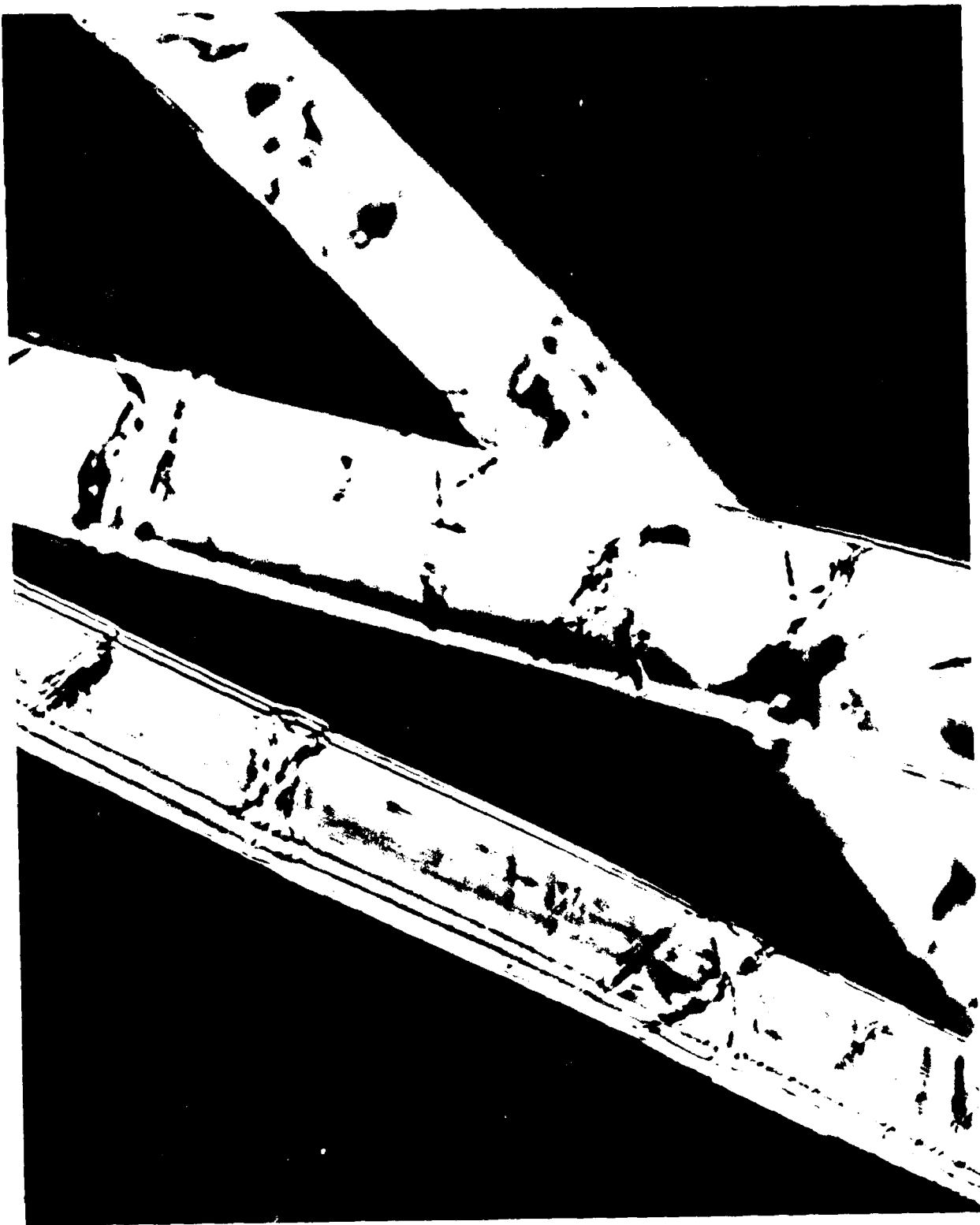


Figure 5. Untreated Spectra 900.



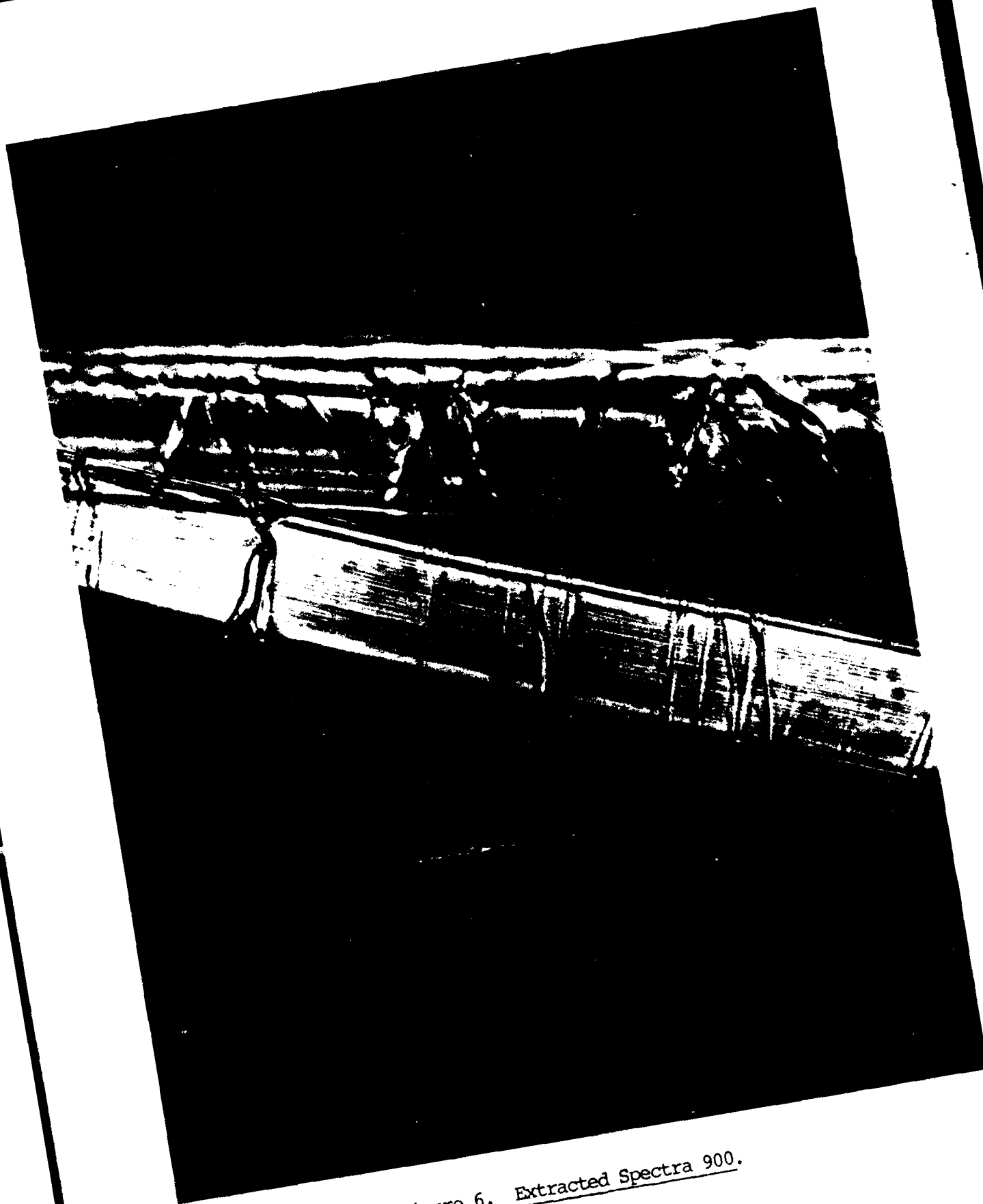


Figure 6. Extracted Spectra 900.

## B. SCF Infusion of Additives into Ultra-High-Density Polyethylene Fibers.

It was of interest to determine the effect of additives, introduced by SCF conditions, on high tensile fibers. Naphthalene was chosen as a trial additive and was expected to infuse into the oriented fiber to act as a lubricant between polymer chains.

The naphthalene-treated Spectra fibers were prepared by immersion in a 10% solution of naphthalene in chloroform. The fibers were withdrawn, air dried, and placed into the supercritical flow apparatus. The temperature of the cell was set to a constant 40°C while carbon dioxide was let into the cell. The pressure reached 1500 psi and was held for five hours. Then the carbon dioxide solvent was slowly bled through the apparatus for an hour while holding the pressure at 1500 psi. The samples were visibly unchanged. The breaking strength of these fibers was similar to that observed with fibers extracted with Freon. In both cases the strength was increased over the control sample. At first we felt the increased strength may have been due to the intended lubrication effect and that naphthalene as well as Freon had penetrated the fiber structure. However, an even greater increase in tensile strength was found for the samples extracted with carbon dioxide. It does not seem likely, in the case of carbon dioxide, that an additive effect is the mechanism responsible. Possibly the fibers under the influence of the supercritical solvent have achieved greater orientation. Another possibility is that the fibers contracted during the SCF treatment and the effective diameter increased.

### C. Supercritical Textile Dyeing Studies

To determine if textile dyeing could be carried out under SCF conditions, a woven sample composed of test strips of various fibers was subjected to SCF carbon dioxide along with several dyes.

The experiment was conducted as follows: A piece of the test fabric (Table 6) was rolled into a tube resting on a piece of glass wool which had the dye deposited on it. The fabric, glass wool and sample were placed into the SCF flow cell (Figure 1 insert) and carbon dioxide was allowed to flow into the cell at a predetermined temperature. The pressure was raised to the desired level and held for various time periods. The outlet was opened slightly at the outset to bleed some of the solvent. The appearance of dye in the exiting solvent indicated that the dye was soluble and mobile within the SCF cell. The actual sample treatment parameters are presented in Table 7.

TABLE 6  
Test Strip Fabrics

Acetate	Acrylan	Arnel-Tricot
Cotton	Creslan	Dacron 54
Dynel	Nylon 6,6	Orlon 42
Silk	Viscose	Wool
Zefran		

TABLE 7  
Sample Dyeing Treatment Parameters

Run	Sample	Dye*	Temp. (°C)	Press. (psi)	Time (h)
1.	TEST STRIP FABRIC	A	50	3000	2
2.	"	A	90	4500	2
3.	"	S	50	3500	2
4.	"	V	60	4500	2
5.	KEVLAR	S	50	3500	2
6.	"	S	50	1450	2

\* Dyes used were: (A) para-toluy1-1,4-diaminoanthraquinone  
(S) Acid Blue 40  
(V) Vat Golden Orange 3G

Of the SCF conditions used in the dyeing study, only the anthraquinone dye, in Run 3 successfully dyed the test strip. The fabric types dyed under these conditions were Zefran<sup>(R)</sup>, Viscose<sup>(R)</sup>, nylon, and Dacron<sup>(R)</sup>.

The Kevlar sample was only stained at the fiber edges but conditions used did not achieve actual dyeing. Other conditions using SCF conditions will be tried under another current project, "Interaction of SCF With Polymers".

#### D. Depolymerization Studies Under Supercritical Fluid Conditions

Previous results indicated that nearly complete depolymerization of polyamides could be achieved in SCF methanol. To further investigate this finding we extended the original experiments to find out what conditions were necessary to totally degrade the polymer and to provide material for full identification of the monomeric products.

The experiments were conducted in a Parr bomb. A sample of polymer was weighed into a glass insert along with 50 mL of solvent and placed inside the bomb. The bomb was sealed and pressurized by externally heating it to the critical temperature. The temperature inside the glass liner and bomb were identical and were maintained throughout the duration of the experiment.

At the specified time the bomb was cooled to room temperature and opened. The contents were filtered, washed with methanol, and analyzed for composition by infrared spectroscopy.

The following Table 8 lists the samples and conditions used in this study.

TABLE 8  
Treatment Schedule for Depolymerization Reactions

Polymer	Solvent	Temp. (°C)	Press. (psi)	Time (h)
1. NYLON 6,6	ACETONITRILE	275	600	2
2. NYLON 6,6	"	245	650	12
3. NYLON 6,6	MEOH	260	1040	2
4. "	"	250	1000	12
5. NYLON 6	"	250	1500	2
6. "	"	250	1500	12
7. POLYETHYLENE TEREPHTHALATE	"	250	1500	12
8. POLYBUTYLENE TEREPHTHALATE	"	250	1450	6
9. POLYCARBONATE	"	250	1400	5
10. KEVLAR	"	250	1450	24

In the runs with nylon 6,6 and acetonitrile as the supercritical solvent, the product was obtained as a solid char mixed with solvent. There was a small amount of flocculent white precipitate suspended in the solvent above the char. The white precipitate was filtered from the char and identified as nylon 6,6 by infrared spectroscopy (KBr, pellet). Apparently this white precipitate is original polymer that had dissolved under supercritical conditions and precipitated out of solution when the reaction was cooled. An infrared scan on the black char material indicated that it was still substantially nylon 6,6 but it had been considerably degraded. We concluded that in these runs the temperature was too high and the primary reaction was thermal degradation of the polymer.

When methanol was used as solvent for nylon 6,6 polymer a dark, gummy residue was formed. In addition, a portion of the polymer had been degraded into products that were identified by infrared as a mixture of monomeric components and oligomers of the nylon polymer. Separation of the reaction mixture was attempted and fractions were collected that were identified as hexamethylene diamine and the corresponding co-monomer, dimethyl adipate. Again the critical temperature of methanol is sufficiently high that thermal degradation processes compete with amide alcoholysis.

Similar results were obtained with nylon 6. With this polymer small amounts of the monomeric ester were obtained along with a large portion of thermally degraded material.

The polyester samples were more amenable to alcoholysis and gave a

very clean reaction. When the bomb was opened white crystals were present in the methanol solvent. These were filtered off. When the filtrate was concentrated and cooled, an additional batch of crystals was collected. The filtrate from this was evaporated to an oil and an infrared spectrum of this oil indicated the presence of the diol monomeric component. The white crystals were identified as methylterephthalate. Yields greater than 50% of methylterephthalate monomer were obtained from both the depolymerization of polybutylene terephthalate and polyethylene terephthalate.

The reaction with Kevlar did not produce appreciable amounts of products although the odor of phenylenediamine could be detected when the reaction vessel was opened. Attempts to isolate the diamine component were not successful. Apparently the conditions in this run were not sufficiently severe to cause methanolysis of the aromatic amide group.

#### E. Polymerization Reactions in Supercritical Fluid Media.

Since it was determined that depolymerization reactions of polyamides and polyesters could be achieved under SCF conditions, it was of interest to investigate whether the equilibrium for depolymerization could be reversed to produce polymeric material. In order for the polymerization condensation reaction to proceed, it was necessary to displace the reaction toward the formation of polymer by removal of the co-reaction product, water. To accomplish this, acetonitrile was used. Hydrolysis of the nitrile under the reaction conditions was expected to utilize the water formed in the polymerization reaction and irreversibly form



acetamide. Polymerization experiments were tried using adipic acid and 1,6-hexanediamine. These conditions are shown in Table 9.

TABLE 9  
Polymerization Reactions Under SCF Conditions

Reactants	Solvent	Temp. °C	PSI	Time	Yield
1. Adipic Acid/1,6 Hexanediamine	CH <sub>3</sub> CN	280	750	2h	>40%
2. " "	"	270	750	0.3h	100%
3. " "	CO <sub>2</sub>	40	2000	2h	—

Runs 1. and 2. gave similar results except that the yield of polymer obtained in the two hour run was less (40%) than in the 20 minute run (100%). This finding indicated that the mechanism to form polymeric material was being complicated by thermal degradation process and that competing reactions were taking place. In both cases a solution was obtained after the reaction. This was evaporated to a solid residue, which was extracted with acetone. The solid was identified by infrared as the expected nylon 6,6 polymer. Solution viscosity measurements on the polymers from both runs indicated that low molecular weight material had been formed.

Reactions that were run in SCF carbon dioxide showed similar results. The infrared spectra of the isolated polymers were less well resolved than that of the polymers prepared in acetonitrile alone; but the appearance of a strong amide band at  $1630\text{ cm}^{-1}$  was distinctly evident. A concern in these reactions was the possible formation of carbamates of the amine monomer; however no evidence for this product was observed in the reaction mixture. Solution viscosity measurements on these polymers were not run.

## V. CONCLUSIONS

Preliminary experiments using supercritical carbon dioxide to extract polymers have shown variable results for tensile tests. All of the extraction runs indicated that very little or no material had been removed from the polymer and that polymer solubility using supercritical carbon dioxide as a solvent was probably not a viable route. In spite of this fact the preliminary tensile test results are sufficiently encouraging to recommend some continuation of work in this area, especially with more appropriate solvents. As an example, it would be useful to study the effects of low molecular weight hydrocarbon solvents like ethane, propane, and butane on the Spectra fibers.

Experiments using additives to the supercritical fluid should be tried with various high performance fibers.

The results with the static supercritical fluid system were promising. The finding that certain polymers could be completely dissolved or depolymerized with a supercritical solvent such as methanol was unexpected and has important implications. Future work in this area

should be carried out to determine optimal conditions and to more fully characterize the depolymerization products observed.

Dyeing under SCF conditions occurred only with the more SCF carbon dioxide soluble anthraquinone dye. The indication here is that with selected SCF soluble dyes, the dyeing process may be possible.

As yet, the experiments to explore the possibility of using supercritical fluids as solvents for polymerization reactions has only scratched the surface of what could be a productive area for research.

As mentioned, work on SCF vinyl polymerization is in progress by other workers. Our experiments were designed to carry out condensation polymerizations and dyeing of fibers in supercritical fluids.

#### LIST OF REFERENCES

1. A. Cifferi and I. M. Ward, Ed., "Ultra High Modulus Polymers", Applied Science Pub., 1979, 323.
2. M. E. Paulaitis, V. J. Krukonis, R. T. Kurnik, and R. C. Reid, "Supercritical Fluid Extraction" Rev. Chem. Eng. 1 1983, 179.
3. Kirk and Othmer, Encyclopedia of Chemical Technology, 3rd Ed. vol. X, 872
4. S.K. Kumar, R.C. Reid, and U.W. Suter, "Precipitation in Supercritical Fluids", Presented at the 192nd American Chemical Society Meeting at Anaheim, California, September 1986.
5. Fed. Standards, Method 4100, July 20, 1978.
6. J.E. Ward and W. Koza, "Hi-Tech Fibers for Improved Ballistic Protection, in Army Science Conference Proceedings volume IV, 265, 17-19 June 1986, West Point, N.Y. (AD A173 682)

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